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Overview on Vapor Feed Direct Methanol Fuel Cell

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Abstract

Direct methanol fuel cell is the best candidate in generating high energy density and compatible as power source for small mobile device. DMFC operate in two basic manners which are active and passive where methanol can be fed in liquid or vapor phase. Passive DMFC is simpler than active DMFC since it operates without using any external devices to deliver methanol and air to the fuel cell. Due to methanol crossover problem faced by liquid feed DMFC operated at high methanol concentration, vapor feed DMFC is an alternative way to solve this problem. Vapor feed DMFC proposed by some groups since it can increase the fuel cell performance and reliable for high methanol concentration. Methanol vapor delivered to the anode by heating the liquid methanol or using a pervaporation membrane. However, there are challenges to overcome such as methanol crossover and water management. Mass transfer resistance should be increased to reduce the methanol crossover and Water management also needed in order to block the water removal from the cathode and thus help to push more water backward from the cathode to the anode in vapor feed DMFC operation to achieve high performance.

Keywords : Vapor feed DMFC; Passive DMFC; Methanol

1. Introduction

Direct methanol fuel cell (DMFC) is an electrochemical energy conversion device which directly converts the chemical energy stored in methanol to electricity. DMFC is considered as the best candidate to replace batteries in micropower applications because of its simplicity, high-specific energy, instantaneous recharging and presumably long life [1]. However, the design of DMFC is still in the prototype stage and its

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commercialization is hindered by several technical challenges such as methanol crossover, low catalytic activity, inadequate water management system, durability and cost [2]. In DMFC, liquid methanol solution supplied actively or passively to the anode electrode either in liquid or vapor phase [3]. This review is focused on a passively operated vapor feed direct methanol fuel cell and the challenges to overcome if high methanol concentration used as the fuel.

2. Active and Passive Direct Methanol Fuel Cell

There are two basic types of DMFC which are active and passive DMFC [4]. Active DMFC operates with the help of external devices such as pump to deliver methanol at the anode and blower to supply air at the cathode side [5]. In passive DMFC, methanol delivered without any external devices and relies on breathing ambient air [6]. The active system has more reliability, gives higher performance and convenient in controlling an operational condition of the fuel cell such as temperature, concentration of methanol and methanol flow rate [4]. In passive systems fuel supply relies on the diffusion of the built in fuel reservoir while ambient air become the source for oxidant [7]. The passive DMFC becomes simpler and more compact which provide a unique feature for the miniaturization of fuel cell [8]. Besides that, parasitic energy losses can be reduces to enhances the overall system efficiency, potentially result in high reliability, low cost, high fuel utilization and high energy density by using a concentrated methanol solution which is favourable in portable device application [9]. Hence, the passive DMFC could be used for low power requirements devices while active DMFC is compatible for higher power devices [10]. Kim et al designed a passive, air-breathing, monopolar DMFC stack [11]. Sun et al developed a new conception of a self-pumping micro-DMFC stack which assembled with metalized polymer bipolar plates. A peak power density of 7.4 mW cm^{-2} was achieved with a 3M methanol solution at ambient air [12]. Shimizu et al studied the design, fabrication and performance evaluation of a completely passive air-breathing DMFC at room temperature. Power density of 11 $mWcm^{-2}$ reached with 4M methanol concentration at current density of 36 $mAcm^{-2}$ [6]. Passive DMFC also can operate with high methanol concentration which was studied by Chan et al. They proposed a new self-regulated passive fuel-feed system and proved that the fuel cell fed with methanol concentration of 12 M gives the same performance as the conventional DMFC with 4 M methanol solution [13]. Table 1 shows the different between active and passive DMFC system.

Table 1. Difference between active and passive DMFC

Active Direct methanol Fuel Cell	Passive Direct Methanol Fuel Cell
1. operate with auxiliary components to deliver methanol at anode and air supplying at cathode	1. operate without any external devices to deliver methanol at anode and supply air at cathode
2. requires large volume and incompatible for portable device application	2. reduced size and allow functionality in portable device
3. very complex and high cost	3. simplicity and low cost
4. convenient in controlling operational condition	4. high energy density by using a concentrated methanol solution

3. Vapor Feed Direct Methanol Fuel Cell

In DMFC, methanol can be fed in liquid or vapor phase. Liquid fed DMFC use a diluted methanol solution and the concentration of methanol for maximum power in a passive DMFC is much higher than in active liquid fed DMFC. However, Ho et al. evaluated the performance of passive liquid fed DMFC and found that the maximum power achieved at 4M of methanol. The performance was slightly decreased at 5M methanol

due to methanol crossover (MCO). A vapor feed direct methanol fuel cell is one of the alternative way to minimize the MCO effect[14]. In the vapor feed DMFC, methanol evaporates from a nearly pure liquid methanol and condensed into a highly dilute methanol solution at the anode side of the fuel cell. Operating mechanism for vapor feed DMFC is characterized by the transport of liquid-gas mixture and protons and the transformation of species by electrochemical reactions. Methanol evaporated by an external heater enters the anode flow channel and condensed in the liquid pad which is connected with the porous gas diffusion layer and next reaches the catalyst layer. Then, it dissociates to protons and electrons within the catalyst layer. Gaseous oxygen reactant passes through the porous gas diffusion layer and reaches the catalyst layer. The oxygen then reacts with electrons and the protons passing across the membrane from the anode [15]. Several methods proposed to vaporize the methanol passively by using membranes that cause a phase change in methanol [16]. There are some advantages by operating in vapor feed such as the cell voltage and power density achieved is higher than in liquid feed [4]. The start-up time for vapor feed is shorter than in liquid feed system due to the mass diffusivity is several orders of magnitude for vapor phase is greater than in the liquid phase. Fukunaga et al suggested a vapor feed DMFC because of its higher activities and the usage of highly concentrated fuel. The water and methanol were supplied with a carrier gas at high temperature and the active components for vapor supply cannot reduce the size of DMFC. In order to increase the energy density and eliminate the active components for fuel supply, passive vapor feed DMFC was proposed [17].

3.1. Passive Vapor Feed Direct Methanol Fuel Cell

Passive vapor feed DMFC which is operate at room temperature and fed with high methanol concentration solutions or neat methanol gains worldwide attention as a promising DMFC technology for mobile power sources [18]. Guo et al used an evaporation pad to deliver pure methanol to the anode with passive thermal or fluids management system. Methanol and water were delivered in two separate wicks. The pure methanol was wicked from liquid methanol reservoir to the evaporation pad. The methanol was evaporated by different heating manners such as electrical heating, catalyst burning and heat recovery from the cell [19]. Jewett et al also developed a vapor feed fuel delivery system for a passive DMFC as shown in Figure 1. Water and methanol that was stored externally and wicked directly to the anode hydrophilic layer and evaporation pad. A maximum power density of 33 mW cm^{-2} is achieved [16].

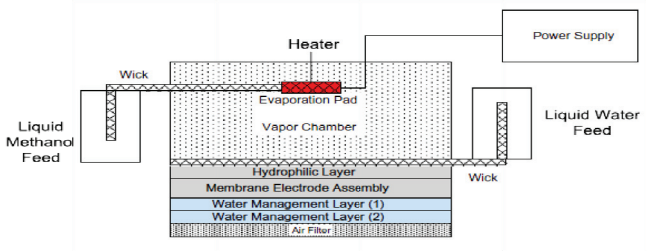

Fig. 1. Schematic of the passive vapour feed system for DMFC

HaeKyoung Kim proposed a passive vapor feed DMFC for mobile application. Pure methanol used in the experiment and vapor was provided to the MEA by a vaporizer, barrier and buffer layer. The result shows the maximum power density obtained was 36 mW cm^{-2} 1.5 times higher energy density compared to liquid feed passive DMFC [20]. Abdelkareem et al. also investigated the performance of passive vapor feed DMFC by using a porous carbon plate (PCP) to deliver methanol vapor to the anode for different methanol concentration. As a result, high methanol concentration over 20 M could be efficiently used to produce power density of

30mW cm^{-2} for more than 10 h [21]. Besides that, Fokkens et al investigated different classes of membranes for their use in methanol vapour fed fuel cells for portable low power applications. Methanol fuel delivered passively using pervaporation membrane. Membranes used in the experiment are perfluorosulfonic acid (PFSA) membranes, sulfonated polysulfone (SPSF) membranes and sulfonated PEEK (SPEEK) membrane. The maximum power density reached was 40 mW/cm^2 at 30 °C. [22]. Fuel cell system based on this pervaporation membrane fuel delivery technology can be completely operate in passive manner as long as water produced in the system can be reused [19]. Table 2 show the previous research done on passive vapour feed DMFC

Table 2. Previous study on passive vapour feed DMFC

Reference	Method of vaporization	Methanol concentration	Maximum power density
Kim. H.K	Methanol vapor is provided through a vaporizer, barrier and buffer layer	-	36 mW/cm^2
Fokkens et al.	Methanol 4apour delivered using pervaporation mambranes (PFSA,SPSF,SPEEK)	-	40 mW/cm^2
Abdelkareem et al	DMFC employed with porous carbon plate (PCP)	2 M to neat	30 mW/cm^2
Jewett et al.	Methanol was evaporated using a thin film electric heater placed inside vapor chamber	-	33 mW/cm^2

4. Challenges of Vapor Feed Direct Methanol Fuel Cell

Vapor feed DMFC need to overcome few major challenges in order to operate in high methanol concentration passively such as methanol crossover through membrane and water management in the fuel cell.

4.1. Methanol Crossover

One of the most challenging problems for the DMFCs that employ Nafion membranes is methanol crossover (MCO) from the anode to the cathode, which causes a mixed potential on the cathode and reduces the overall cell voltage [13]. Several methods were introduced to overcome this problem. Kim et al. used a hydrogels in a methanol fuel cartridge as a diffusion-rate-controlling agent that suppressed MCO in passively operated liquid fed DMFC. Vapor phase operation did not specified but probably most of the liquid methanol that soaked into the hydrogel was in vapor-liquid equilibrium [23]. Nakagawa et al. employed a hydrophobic porous carbon plate with a high transfer resistance between the fuel reservoir and the anode current collector to reduce the methanol delivery rate. Optimized design of the porous plate cause the methanol-crossover rate significantly reduced and their passive DMFC can run with 22.0 M methanol solution without reducing the cell performance[24]. For a vapor feed DMFC that operates with neat methanol as fuel, the MCO is so high and thus a very thick methanol barrier layer is required to decrease the methanol crossover rate. Instead of employing a methanol barrier layer, other approaches such as decreasing the open ratio of the vaporizer and adding a gas mixing layer between the fuel reservoir and the MEA in vapor feed DMFC [2].

4.2. Water Management

Depletion of water inside the anode catalyst layer, especially at higher current densities will reduce the performance of the fuel cell [25]. In vapor feed DMFC, back flow of water from cathode to anode act as water supply to hydrate the electrolyte membrane [26]. For vapor feed DMFC fed with neat methanol, water needed for methanol oxidation reaction supplied passively from the cathode through the membrane by diffusion. The

anode performance depends water transport flux from the cathode to the anode as well as the water concentration in the anode catalyst layer [27]. Xu et al studied the effect of different water management approaches by the addition of a water management layer (WML) and a hydrophobic air filter layer (AFL) for a passive vapor-feed DMFC which lowered the internal resistance and thus improve th performance. Hydrophobic WML blocked the water removal from the cathode and thus helped to push more water backward from the cathode to the anode, leading to a better membrane hydration and a lower internal resistance [18]. Masdar et al. fixed a hydrophobic air filter (HAF) in the vapor feed DMFC operated with a high concentration of methanol. The HAF increases the water back diffusion from the cathode to the anode and provide a space from the cathode surface to increase water crossover and the current density [28]. A novel approach was proposed by Li et al. to improve the water management of passive vapor-feed DMFC fed with neat methanol by adopting perforated covers with different open ratios at the cathode [2]. Besides that, Wu et al. investigated the effect of the design parameters of the membrane electrode assembly (MEA) and operating conditions on the water transport in a DMFC operating with neat methanol. Thinning the anode gas diffusion layer (GDL) and the membrane as well as thickening the cathode GDL can enhance the water transport flux from the cathode to the anode[27].

5. Conclusion

By operating the passive vapor feed DMFC, high performance can be achieved and the structure is simpler than active DMFC. However, methanol crossover and water management problems occur in passive vapor feed DMFC with high methanol concentration fed. Employing a porous material at the anode or methanol barrier layer used to increase the mass transfer resistance in the fuel cell hence reduce MCO. Water management layer was added at the cathode to push more water backward from cathode to anode to hydrate the membrane for methanol oxidation reaction.

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